

Restriction of the Environment of the Dimethylthallium(III) Ion by 'Threading' through a Crown Ether: X-Ray Crystal Structure of Dimethyl(dibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclo-octadecin)-thallium(III) 2,4,6-Trinitrophenolate

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The X-ray crystal structure of the title compound shows that the linear dimethylthallium(III) ion is threaded through the crown ether, with the TlC_2 unit held perpendicularly to the plane containing the six ether oxygen atoms and the thallium atom.

Multinuclear magnetic resonance parameters of diorganothallium(III) derivatives depend in a complex manner on solvent and anion effects.¹ In an effort to minimize these effects by restriction of the equatorial environment of the linear dimethylthallium(III) ion, we have synthesized a range of compounds in which the ion is complexed with 18-crown-6 ethers. The X-ray crystal structure of one of these compounds, dimethyl(dibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclo-octadecin)thallium(III) 2,4,6-trinitrophenolate, (**1**) clearly establishes that the linear $[\text{Tl}(\text{CH}_3)_2]^+$ ion is threaded through the dibenzo-18-crown-6 ether to form a complex cation (Figure 1). There are no significant interactions between the cation and the picrate anion [the shortest interionic contacts involving O are O(picrate) . . . H(crown), 2.40; O(picrate) . . . O(crown), 3.17; O(picrate) . . . C(crown), 3.07 Å]. The TlO_6 atoms are planar to within 0.09 Å and the TlC_2 unit is perpendicular to

this plane. The thallium atom lies at the centre of an O_6 hexagon which is slightly elongated in the direction of each benzene ring. Consequently, the Tl-O distances for O(6), O(15) [2.698(9), 2.694(10) Å, respectively] are shorter than those for oxygen atoms adjacent to the benzene rings (2.769—2.818 Å).

The interaction between $[\text{Tl}(\text{CH}_3)_2]^+$ and the crown ether as the cation threads through the crown ether cavity would appear to be substantial. The dimensions of the O_6 hexagon (average diagonal, $d = 5.511$ Å) are similar to those in the Rb^+ complex with dibenzo-18-crown-6 ($d = 5.502$ Å)² and allowance for the van der Waals' radius of O (1.4 Å)³ leaves a cavity of 2.7 Å, to be compared with the van der Waals' diameter of the $[\text{Tl}(\text{CH}_3)_2]^+$ cylinder, 4.0 Å (van der Waals' radii; Tl,⁴ 1.96; CH_3 ,³ 2.0 Å). However the extent of interaction suggested by this comparison is likely to be reduced as

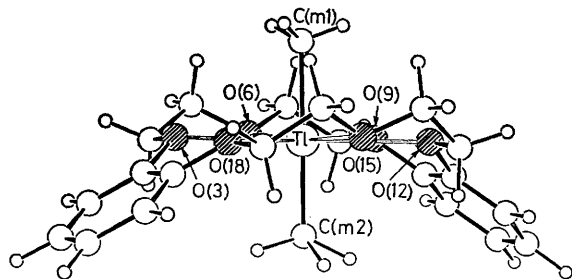


Figure 1. The structure of $[\text{Ti}(\text{CH}_3)_2(\text{dibenzo-18-crown-6})]^+$, (**1**). Internuclear distances: $\text{Tl}-\text{C}(\text{m}1)$, 2.180(17); $\text{Tl}-\text{C}(\text{m}2)$, 2.110(18); $\text{Tl}-\text{O}(3)$, 2.791(8); $\text{Tl}-\text{O}(6)$, 2.698(9); $\text{Tl}-\text{O}(9)$, 2.818(11); $\text{Tl}-\text{O}(12)$, 2.769(8); $\text{Tl}-\text{O}(15)$, 2.694(10); $\text{Tl}-\text{O}(18)$, 2.770(11) Å. Angle: $\text{C}(\text{m}1)-\text{Tl}-\text{C}(\text{m}2)$, 178(1)°.

a consequence of the different conformation probably adopted by the flexible free crown ether² and possibly resulting in an increased cavity for the free ligand. During the initial stages of threading, the crown ether probably interacts with the $[\text{Ti}(\text{CH}_3)_2]^+$ ion through dipole-dipole interactions between the ether oxygen atoms and the methyl group, guiding the cation into the crown cavity. A precursor for this process appears to be shown by the structure of the complex between dimethyl acetylenedicarboxylate and 18-crown-6⁵ where an ester methyl group closely approaches the O_6 plane with distances between ether-oxygens and the methyl group which are substantially less than the van der Waals' contacts. The nature of the remaining part of the potential guest molecule does not allow the methyl group to thread through the crown cavity. Support for the importance of these interactions in the threading process may be provided by noting that the linear uranyl ion, $[\text{UO}_2]^{2+}$, does not thread through 18-crown-6.^{6,7} Here, the initial ether-cation $\text{O} \cdots \text{O}$ interactions would be repulsive, although other factors⁶ may be responsible for non-threading.

The crown ether adopts a *syn* conformation with the least-squares planes of the phenyl rings inclined at 39 and 144°, respectively, to the O_6 plane. Similar conformations have been observed for Na^+ and Rb^+ complexes.^{2,8} The slightly different $\text{Tl}-\text{C}$ bond lengths in (**1**) may reflect the interactions resulting from this arrangement. Unequal values for $^2J(\text{Tl}-\text{H})$ in $[\text{Ti}(\text{CH}_3)_2]^+$ have previously been used to suggest⁹ that the cation is held perpendicularly to, and at the centre of, the O_6 plane in the related complex (**2**) with *cis-syn-cis*-dicyclohexyl-18-crown-6 (isomer A).⁹ The ^1H n.m.r. spectrum of (**1**),

in pyridine solution, shows only one methyl environment, indicating that the conformation of the crown ether may be changing rapidly (*syn* \rightleftharpoons *anti* \rightleftharpoons 'inverted' *syn*, etc.) on the n.m.r. timescale, whereas conformational changes in *cis-syn-cis*-dicyclohexyl-18-crown-6 cannot equalize the methyl environments.

Complex (**1**) was prepared from dimethyl(2,4,6-trinitrophenolato)thallium(III)⁹ and dibenzo-18-crown-6 by a method similar to that described for the dicyclohexyl-18-crown-6 complex⁹ but using methanol as solvent. Crystals suitable for X-ray analysis were obtained from dimethyl sulphoxide solution.

Crystal data: (**1**), $\text{C}_{28}\text{H}_{32}\text{N}_3\text{O}_{13}\text{Tl}$, $M = 822.97$, triclinic, space group $P\bar{1}$, $a = 14.440(3)$, $b = 11.202(3)$, $c = 11.087(2)$ Å, $\alpha = 80.06(2)$, $\beta = 112.02(3)$, $\gamma = 61.43(2)^\circ$, $U = 1552$ Å³, $D_c = 1.76$ g cm⁻³, $Z = 2$, θ -range 3–25°, $R = 0.053$ for 2955 data with $I > 3\sigma(I)$ obtained on a Philips PW1100 diffractometer with $\text{Mo-K}\alpha$ radiation. Absorption corrections were applied.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.